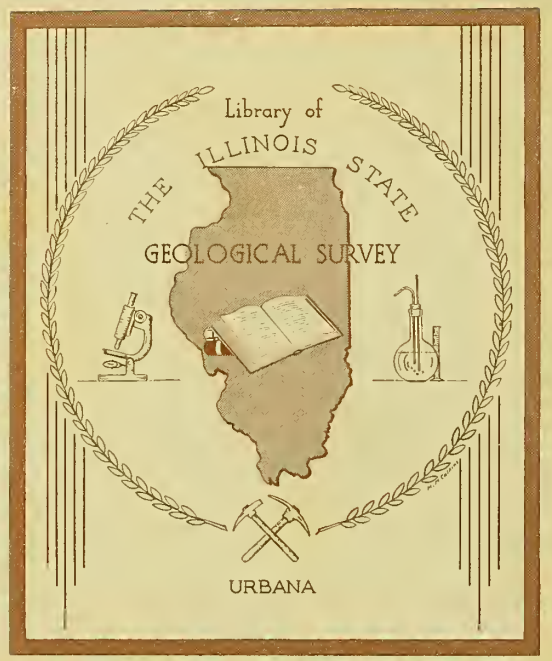

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SURVEY OF ILLINOIS CRUDE OILS FOR TRACE CONCENTRATIONS OF MERCURY AND SELENIUM

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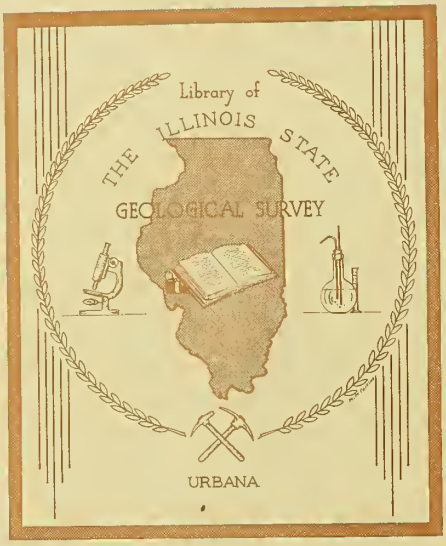
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SURVEY OF ILLINOIS CRUDE OILS FOR TRACE CONCENTRATIONS OF MERCURY AND SELENIUM

R. F. Mast and R. R. Ruch

ABSTRACT

Forty-six samples of Illinois crude oil were tested for trace concentrations of mercury and selenium by neutron activation analysis techniques. The samples were selected to represent the largest oil pools, all the major oil producing strata in the state, and the range of gravity of the oil and depth to production.

In 43 of the samples analyzed, mercury, if present, was below the usual limits of detection of the analytical method, i.e., < 0.02 to < 0.04 micrograms per milliliter (μg/ml). Although mercury was not positively detected, larger than usual detection limits were reported for the other three samples because of interference due to the presence of from 0.2 to 0.4 μg/ml of selenium. A mean of 0.14 μg/ml of selenium was found for eight of the 46 samples. Selenium was not detected (< 0.04 μg/ml) in the other 38 samples.

Minute quantities of volatile materials inherent in fossil fuels can adversely affect the quality of the environment when the fuels are consumed. Mercury (Hg) and selenium (Se) are two such materials. To determine whether Illinois crude oils contain these two elements, samples of crude from Illinois wells were subjected to neutron activation analysis.

SAMPLING PROGRAM

Samples of oil were collected from individual wells throughout the state's producing areas rather than at pipeline terminals. Although pipeline samples would have represented all the oils of a particular area, thus making

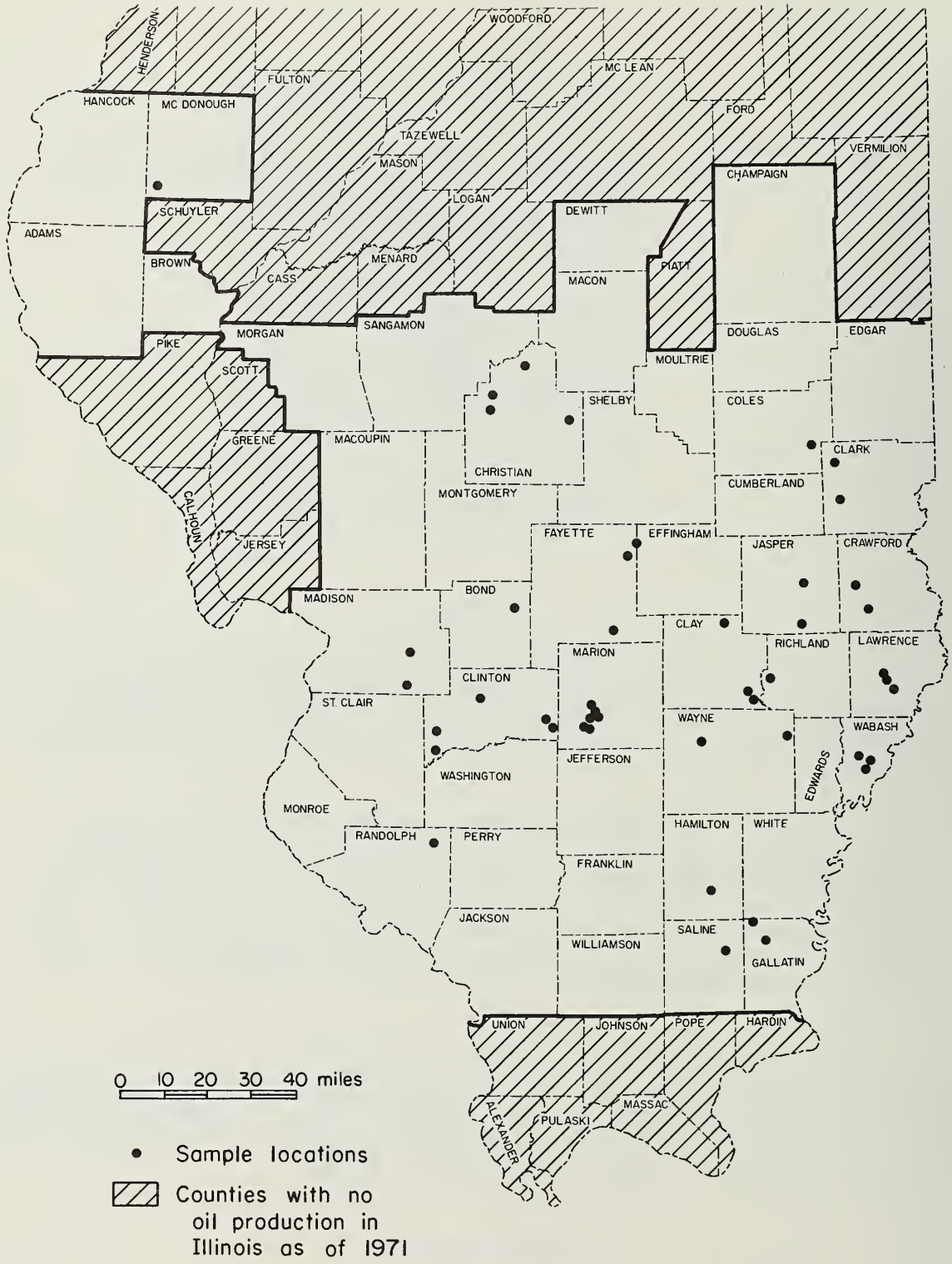

Fig. 1 - Distribution of locations from which samples were taken.

fewer samples necessary for the survey, they have two disadvantages. First, out-of-state oil is mixed with Illinois crude in some pipelines, which would make samples from them unacceptable for the tests and thus leave the areas from which those pipelines draw oil unrepresented in the survey. Second, emulsion breakers or other substances are added to crude oils to prepare them for sale to pipelines, and such additives can complicate analysis of the oils.

The individual samples were taken in all the major producing zones in the 10 largest oil producing fields in Illinois. Additional samples were then chosen to ensure representation of all the major stratigraphic intervals from which oil is produced in the state. Other samples were added to provide more complete ranges of gravity and producing depths and to cover oil producing areas not already represented. In all, 46 samples of Illinois crude oil were taken for analysis.

The samples proved to be adequately representative of the oil produced in the state, as is shown in table 1. They covered essentially the entire range of gravities and reservoir depths of Illinois crude oil. They also represented fields from which 72 percent of the state's total oil production came in 1971. Although not all the pays in these fields were sampled, the most significant of them were. Fifty percent of the total productive acreage of the state also was represented by the samples (table 1).

TABLE 1—COMPARISON OF PRESENT SAMPLE DATA WITH PREVIOUS DATA FOR ALL ILLINOIS RESERVOIRS

	Samples in this study		All Illinois oil reservoirs*	
	Mean	Range	Mean	Range
Crude oil gravity (°API)	36.8	24.2 - 43.2	36.8	24 - 44.9
Reservoir depth (ft)	2242	438 - 4492	2000	215 - 5450
	Oil fields sampled		Illinois	
Total 1971 oil production	28,038,000 bbl		39,084,000 bbl	
	Pools sampled		Illinois	
Pay area	368,000 acres		750,000* acres	

* Estimated from 1969 data in Mast, 1970.

Table 2 shows the distribution of sampling in the various stratigraphic intervals. Some stratigraphic intervals were preferentially sampled to obtain comprehensive geographic and stratigraphic coverage of the producing areas of the state.

The geographic locations where the samples were taken are shown in figure 1. As the figure shows, the productive areas of the state were adequately covered. The samples, therefore, are representative of oil production in Illinois and can be used with confidence for the mercury and selenium

TABLE 2—STRATIGRAPHIC DISTRIBUTION OF SAMPLES

Stratigraphic interval or pay zone	Samples	Percentage of Illinois reservoir volume
Pennsylvanian	3	22.9
Mississippian		
Kinkaid-Beech Creek (Barlow)	1	5.5
Cypress	5	17.5
Paint Creek	3	12.8
Aux Vases	6	16.6
Ste. Genevieve	7	15.3
St. Louis - Borden (Carper)	5	2.3
Devonian	5	3.4
Silurian	7	2.1
Galena (Trenton)	4	1.6
TOTAL	46	100.0

analyses. The same set of samples could also be used for future studies of other trace elements in oil.

A few samples were taken from the stock tank, but most were collected at the well head from the bleeder valve. Before the samples were taken, the bleeder valve was flushed and the sample jar and plastic collecting bucket were rinsed with the well fluid. A new bucket was used for each sample.

The plastic buckets were pierced near the bottom by a hole three-eighths of an inch in diameter that served to separate the produced water from the oil. The samples were stored in wide-mouthed glass jars with hard plastic screw tops. A sheet of Parafilm was sealed between the jar and its top to prevent contamination of the sample from the lid.

ANALYTICAL PROCEDURE

About 12 ml of crude oil, which had been gently agitated with deionized water and allowed to settle for a day, was placed in a 4-dram polyethylene snap-cap container that had previously been cleaned with deionized water and acetone. The container was then heat sealed and irradiated with comparitor standards for 2 hours in a thermal neutron flux of 1.4×10^{12} neutrons cm^{-2} sec^{-1} in the University of Illinois Research Reactor Facility. About an hour

after irradiation, 10.0 ml of the sample was transferred to a 2-ounce bottle with a plastic-lined cap. The samples were stored for a month to allow the shorter lived radioactivity to decay away preferentially before we attempted to count the 47-day half-life radioactivity of ^{203}Hg. All samples and standards were counted under identical conditions for 900 minutes at optimum geometry with a 3-inch by 3-inch NaI (Tℓ) detector connected to a 400-channel analyzer. The 0.28 Mev photopeak area of ^{203}Hg was used for identification and quantitative determination of mercury.

Samples that showed a definite peak above the general background were counted again after about 40 days to confirm the half-life. The photopeaks of standards containing known amounts of mercury and selenium (as dissolved salts in dilute acid solution) were compared directly with photopeaks of our samples for quantitative estimation.

If no photopeak was discernible above background, a "theoretical" photopeak height equivalent to at least 10 percent of the background height was used for the limit of detection for that sample, and the calculated value was reported as "less than" (<). This means that no mercury concentration above that value was present. However, mercury may be present in concentrations below the calculated value or may be totally absent.

In a few samples ^{75}Se photopeaks were present. Three photopeaks (0.14, 0.27, and 0.40 Mev) were used for identification and quantitative determination of the element. The presence of ^{75}Se at 0.27 Mev interfered with the detection of ^{203}Hg at 0.28 Mev. When selenium is present, the height of the ^{75}Se photopeak at 0.27 Mev is calculated as the upper limit at which mercury might be detected. The fact that the photopeak was almost totally due to selenium strongly suggests that the reported "less than" value for mercury would be further diminished if no selenium were present.

Longer irradiation at higher fluxes would have given better counting statistics and would have increased the observed limits of detection. The use of high-resolution Ge(Li) detectors also would have more accurately distinguished ^{203}Hg from ^{75}Se and afforded better sensitivity. However, the sensitivities ($\sim$0.02 to 0.04 ppm for mercury and $\sim$0.04 ppm for selenium) were adequate for determining whether or not *significant* amounts of mercury (and possibly selenium) are present in Illinois crude oils.

RESULTS

Table 3 (arranged in stratigraphic order) gives the results of the analyses, the oil gravity, and reservoir depth for the 46 crude oil samples. In 43 (93 percent) of the samples listed in table 3, mercury concentrations were below the usual detection limits of 0.02 to 0.04 µg/ml. In fact, mercury may be present in concentrations below the reported "less than" values or may not be present at all. In the other three samples the limit of detection was higher than normal (up to 0.2 µg/ml) because of the interfering effect of the selenium present. Selenium was actually detected in eight samples, but in five of them its concentration was so low that it did not significantly influence the mercury detection limits. The mean selenium concentration for

TABLE 3—MERCURY AND SELENIUM CONTENT OF ILLINOIS (°API) CRUDE OILS

Stratigraphic interval or pay zone	Sample	Limit of detection or concentration (µg/ml)* Hg	Se	Gravity of crude (°API)	Depth (ft)	Lithology†
Pennsylvanian	0-1673	< 0.04	0.08	35.4	890	S
	0-1696	< 0.03	0.06	24.2	479	S
	0-1697	< 0.02	< 0.04	32.0	950	S
Kinkaid-Beech Creek (Barlow)	0-1850	< 0.02	< 0.04	38.0	2125	S
Cypress	0-1666	< 0.03	< 0.04	34.6	2617	S
	0-1669	< 0.03	< 0.04	40.0	1400	S
	0-1671	< 0.02	< 0.04	36.0	1545	S
	0-1840	< 0.01	< 0.04	35.0	2308	S
	0-1841	< 0.01	< 0.04	35.2	858	S
Paint Creek	0-1768	< 0.03	< 0.04	35.0	1600	S
	0-1672	< 0.02	< 0.04	37.8	1511	S
	0-1678	< 0.04	< 0.04	37.0	1719	S
Aux Vases	0-1667	< 0.02	< 0.04	39.0	2921	ST
	0-1679	< 0.03	0.06	37.0	1718	ST
	0-1766	< 0.04	< 0.04	39.0	3150	ST
	0-1769	< 0.02	< 0.04	32.0	2880	ST
	0-1842	< 0.01	< 0.04	38.2	2628	ST
	0-1843	< 0.01	< 0.04	38.0	3138	ST
Ste. Genevieve	0-1668	< 0.02	< 0.04	40.0	2963	OL
	0-1670	< 0.09	0.2	33.0	1860	OL
	0-1677	< 0.02	< 0.04	40.0	2806	OL
	0-1680	< 0.04	0.07	35.0	2020	OL
	0-1767	< 0.03	< 0.04	38.0	3170	OL
	0-1845	< 0.02	< 0.04	35.0	2597	OL
	0-1846	< 0.02	< 0.04	38.2	2796	OL
St. Louis-Borden (Carper)	0-1684	< 0.02	< 0.04	39.0	2966	L
	0-1685	< 0.02	< 0.04	38.0	3250	L
	0-1690	< 0.04	0.08	37.2	1352	ST
	0-1694	< 0.2	0.4	37.0	2160	L
	0-1847	< 0.02	< 0.04	36.0	3249	ST

(Continued on next page)

TABLE 3—Continued

Stratigraphic interval or pay zone	Sample	Limit of detection or concentration (µg/ml)* Hg	Se	Gravity of crude (°API)	Depth (ft)	Lithology†
Devonian	0-1681	< 0.02	< 0.04	38.4	2291	L
	0-1682	< 0.03	< 0.04	37.4	2865	L
	0-1686	< 0.02	< 0.04	35.2	438	S
	0-1687	< 0.02	< 0.04	38.6	1793	DS
	0-1692	< 0.07	0.2	35.2	3303	L
Silurian	0-1764	< 0.02	< 0.04	37.0	1890	L
	0-1770	< 0.03	< 0.04	40.6	1932	L
	0-1771	< 0.03	< 0.04	39.4	1928	L
	0-1772	< 0.02	< 0.04	40.4	2143	L
	0-1773	< 0.02	< 0.04	35.2	2184	L
	0-1804	< 0.02	< 0.04	35.2	1733	L
	0-1849	< 0.02	< 0.04	33.0	1677	L
Galena (Trenton)	0-1683	< 0.02	< 0.04	43.2	3976	L
	0-1691	< 0.02	< 0.04	40.0	2341	L
	0-1693	< 0.02	< 0.04	37.0	4492	L
	0-1695	< 0.02	< 0.04	38.2	2390	L

*< = not detected, less than stated value. † S, sandstone; ST, siltstone; OL, oolitic limestone; L, limestone; DS, sandy dolomite.

the eight samples was 0.14 µg/ml, and values ranged from 0.06 to 0.4 µg/ml. This compares with a mean of 0.13 ppm selenium that was found by Pillay, Thomas, and Kaminski (1969) in two samples of Illinois crude oil. Selenium was not detected (< 0.04 µg/ml) in the other 38 samples.

Data were not reported for four of the original 46 samples, in which low (0.05 to 1 µg/ml) levels of mercury were positively detected. Reruns of the same samples in the laboratory confirmed the original analytical data. Because these results were so unusual, the same four wells were sampled a second time, but in the new samples no mercury was detected. At one of the wells from which the samples had been taken, samples of the two chemicals used in that well during production operations—a corrosion inhibitor and a demulsifying agent—and a sample of the produced water were also collected, but neither the chemicals nor the water contained detectable amounts of mercury. We concluded from these data that the source of mercury was not in the reservoir oil and that the original four samples had somehow been contaminated. Consequently, table 3 reports data from the second set of crude samples only. Although we feel certain that the mercury in the four samples was the result of contamination, we could not identify its source.

TABLE 4—MERCURY AND SELENIUM CONTENTS OF OILS AND COALS

Region	Fuel	Samples	Hg range (μg/g)	Se range (μg/g)
California*	oil	4	0.077 - 29.7	0.151 - 1.4
Libya*	oil	3	0.062 - 2.1	0.219 - 1.1
Illinois†	oil	46	< 0.01 - < 0.2	< 0.04 - 0.4
Eastern U.S.‡	coal	7	0.07 - 0.41	---
Western U.S.‡	coal	4	0.05 - 0.16	---
Illinois⁂	coal	23	0.09 - 0.52	1.2 - 7.7

* Shah, Filby, and Haller, 1970.
† This study.
‡ Schlesinger and Schultz, 1972.
⁂ Ruch, Gluskoter, and Shimp, 1973.

DISCUSSION

Table 3 reveals no correlations between any of the chemical data and the stratigraphy, crude oil gravity, or depth, possibly in part because no exact values for mercury below the detection limits could be determined.

Table 4 summarizes some of the published data on mercury and selenium in oil and coal. Although the available data are very limited for areas outside of Illinois, the table does provide some basis for comparing the mercury and selenium concentrations in Illinois oils with those in coal and in oils from other areas. Mercury and selenium concentrations in Illinois crude oils proved to be exceptionally low, very much lower than those in crudes from Libya or California and still lower than concentrations found in coal from various parts of the United States.

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